

CLAIMS

1. A process for producing a lower aliphatic
carboxylic acid ester, comprising reacting a lower alcohol
5 and a lower aliphatic carboxylic acid in a gas phase in the
presence of a catalyst, wherein said catalyst comprises an
inorganic support having supported thereon at least one
heteropolyacid and/or heteropolyacid salt.

2. A process as claimed in claim 1, wherein the
10 inorganic support is at least one member selected from the
group consisting of silica, alumina, silica alumina and
zeolite.

3. A process as claimed in claim 2, wherein silica is
silica gel comprising at least SiO_2 in an amount of 90% by
15 mass or more.

4. A process as claimed in claim 1, wherein the sum
total of the heteropolyacid and/or a salt thereof supported
is from 50 to 1,000 g based on 1 liter of the inorganic
support before the loading of heteropolyacid and/or
20 heteropolyacid salt.

5. A process as claimed in claim 1, wherein the
heteropolyacid is selected from the group consisting of the
following heteropolyacids:

| | |
|-------------------------------|--|
| tungstosilicic acid | $H_4 [SiW_{12}O_{40}] \cdot xH_2O$ |
| tungstophosphoric acid | $H_3 [PW_{12}O_{40}] \cdot xH_2O$ |
| molybdophosphoric acid | $H_3 [PMo_{12}O_{40}] \cdot xH_2O$ |
| molybdosilicic acid | $H_4 [SiMo_{12}O_{40}] \cdot xH_2O$ |
| vanadotungstosilicic acid | $H_{4+n} [SiV_nW_{12-n}O_{40}] \cdot xH_2O$ |
| vanadotungstophosphoric acid | $H_{3+n} [PV_nW_{12-n}O_{40}] \cdot xH_2O$ |
| vanadomolybdophosphoric acid | $H_{3+n} [PV_nMo_{12-n}O_{40}] \cdot xH_2O$ |
| vanadomolybdosilicic acid | $H_{4+n} [SiV_nMo_{12-n}O_{40}] \cdot xH_2O$ |
| molybdotungstosilicic acid | $H_4 [SiMo_nW_{12-n}O_{40}] \cdot xH_2O$ |
| molybdotungstophosphoric acid | $H_3 [PMo_nW_{12-n}O_{40}] \cdot xH_2O$ |

wherein n is an integer of 1 to 11 and x is an integer of 1 or more.

6. A process as claimed in claim 1, wherein the heteropolyacid salt is selected from the group consisting of lithium, cesium, potassium, sodium, magnesium, barium, copper, gold, gallium and ammonia salts of at least one of the following heteropolyacids:

| | |
|-------------------------------|--|
| tungstosilicic acid | $H_4 [SiW_{12}O_{40}] \cdot xH_2O$ |
| tungstophosphoric acid | $H_3 [PW_{12}O_{40}] \cdot xH_2O$ |
| molybdophosphoric acid | $H_3 [PMo_{12}O_{40}] \cdot xH_2O$ |
| molybdosilicic acid | $H_4 [SiMo_{12}O_{40}] \cdot xH_2O$ |
| vanadotungstosilicic acid | $H_{4+n} [SiV_nW_{12-n}O_{40}] \cdot xH_2O$ |
| vanadotungstophosphoric acid | $H_{3+n} [PV_nW_{12-n}O_{40}] \cdot xH_2O$ |
| vanadomolybdophosphoric acid | $H_{3+n} [PV_nMo_{12-n}O_{40}] \cdot xH_2O$ |
| vanadomolybdosilicic acid | $H_{4+n} [SiV_nMo_{12-n}O_{40}] \cdot xH_2O$ |
| molybdotungstosilicic acid | $H_4 [SiMo_nW_{12-n}O_{40}] \cdot xH_2O$ |
| molybdotungstophosphoric acid | $H_3 [PMo_nW_{12-n}O_{40}] \cdot xH_2O$ |

wherein n is an integer of 1 to 11 and x is an integer of 1 or more.

7. A process as claimed in claim 1, wherein the lower alcohol and the lower aliphatic carboxylic acid are reacted in a gas phase in the presence of water and said catalyst.

8. A process as claimed in claim 7, wherein the concentration of water is from 1 to 10 mol% based on the total molar number of the lower aliphatic carboxylic acid and the lower alcohol.

9. A process as claimed in claim 1, wherein the conversion of the lower alcohol is 70% by mass or more.

10. A process as claimed in claim 1, wherein the ratio of the lower alcohol to the lower aliphatic carboxylic acid is in the range of lower alcohol : lower aliphatic carboxylic acid = 1:10 to 1:1 in terms of the molar ratio of the sum totals of respective components.

11. A process as claimed in claim 1, wherein the lower alcohol contains at least one of an olefin and a diether corresponding to the dehydrated products of the lower alcohol.

12. A process as claimed in claim 1, wherein the lower alcohol is selected from the group consisting of methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, isobutanol, tert-butanol, allyl alcohol and crotyl alcohol.

13. A process as claimed in claim 1, wherein the lower aliphatic carboxylic acid is selected from the group

consisting of formic acid, acetic acid, propionic acid,
acrylic acid, methacrylic acid and butyric acid.

14. A process as claimed in claim 1, wherein the lower
alcohol is ethanol and the lower aliphatic carboxylic acid is
acetic acid.